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Resonance photoionization of a diarylethene derivative in the presence of cyclodextrins using multi-color multi-laser irradiation



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ABSTRACT

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Keywords: Diarylethene Photoionization Cyclodextrin Multiple laser irradiation Flash photolysis Photochromism Photochromism is isomerization of a molecule induced by light, and is attractive for applications like actuators and optical memory. However, the photodynamics of photochromic materials under excitation by three lasers at three different wavelengths are poorly understood. In this article, we investigate the properties of the well-known photochromic material 2,3-bis(2,4,5-trimethyl-3-thienyl) maleic anhydride (1) upon excitation by one, two and three lasers. In these experiments, α -, β - and γ -cyclodextrin (CD) are added to 1 to form inclusion complexes to improve the solubility of 1 in water/acetonitrile. First, the formation of 1/CD inclusion complexes is evaluated by changes in the ¹H NMR spectrum of 1 and calculations. We find that the area of each molecule of 1 in the 1/CD inclusion complexes exposed to the solvent depends on the cavity size of the CD, and that the CD also affects the ratio of the antiparallel and parallel conformations of the open form (OP) of **1**. The transient absorption of hydrated electrons in the 1/CD systems is then observed at 720 nm by flash photolysis using one laser (266 nm), two lasers (266 and 532 nm) and three lasers (266, 532 and 355 nm). The ionization quantum yields of 1 depend on both the type of CD present, which is rationalized by the ability of 1 to isomerize in the different-sized cavities of α -, β - and γ -CD, and on the laser pulse configuration. The ionization efficiency obtained using the twolaser system is higher than that measured with the one-laser system. This confirms that two-photon ionization of **1** proceeds through two-step two-photon excitation with $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_n$ singlet-state transitions. The photoionization efficiency of 1 in the presence of CDs determined using three laser pulses increases upon opening of the closed-ring isomer (CL) of **1** by 532 nm irradiation (the second laser pulse). This effect is particularly obvious in the presence of γ -CD. This investigation of the photodynamics of **1** in inclusion complexes using multiple lasers contributes to our understanding of how we can influence photochromism using host species and different laser wavelengths.

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1. Introduction

Photochromism is a photoinduced reversible isomerization between two forms of a chemical species and has attracted much attention from a fundamental viewpoint and for potential applications in optoelectronic devices such as optical memory, switches, and actuators [1–4]. Among the various photochromic materials, diarylethene derivatives with heterocyclic rings are thermally stable as well as being highly sensitive to photostimuli, displaying quantitative reversible supramolecular transformations that are triggered by light irradiation [5]. Some of these materials

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are not thermochromic even at 150 °C, and adequate photochromic performance can be maintained for more than 10⁴ cycles [1,6–12].

2,3-Bis(2,4,5-trimethyl-3-thienyl) maleic anhydride (1), as shown in Scheme 1, is a well-known photochromic diarylethene derivative with thiophene rings. The photochromism of 1 is attractive for application in optical switching devices and polymer films [13–15]. The cyclization process of 1 in solution has been investigated using picosecond laser photolysis, which revealed that the photochromic reaction of 1 is influenced by solvent viscosity and polarity [16–18]. Additionally, the two-photon photochromism of 1 can be modulated by Förster resonance energy transfer from fluorene derivatives that can absorb two photons [19].

Single- or multiphoton photochromic reactions can take place in the crystalline phase and organic solutions of diarylethene derivatives upon two-laser irradiation [20,21]. The two-photon ionization (TPI) of organic compounds proceeds through a twostep excitation from the S_0 to the S_1 state and from the S_1 to the S_n

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Scheme 1. Photochromism of 2,3-bis(2,4,5-trimethyl-3-thienyl) maleic anhydride (1).

state. The photoionization probability of TPI depends on the electronic character of the S_1 and S_n states (this is controlled by the stilbene in diarylethene derivatives), as well as the electronic conformation of the radical cation [22–24]. Several groups, including our own, have studied the TPI of a series of organic molecules from which an electron is removed and attached to the nearest solvent molecule [22,24–26]. The dependence of the concentration of the radical cation generated by TPI on the solvent, fluorescence lifetime, oxidation potential of the molecules, and laser wavelength and intensity has been determined [24,26].

The absorption of the $S_0 \rightarrow S_1$ transition is different from that of the $S_1 \rightarrow S_n$ transition, so $S_0 \rightarrow S_1 \rightarrow S_n$ transitions can be selectively induced by excitation using a two-color two-laser system tuned to the $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_n$ transitions [27–31] to a greater extent than by a one-laser system tuned to the $S_0 \rightarrow S_1$ transition, which is generally used for TPI. As a further extension of this, the three-color three-laser photochemistry of di(*p*-methoxyphenyl) methyl chloride and the stepwise photocleavage of the C—O bonds of bis (substituted-methyl) naphthalenes have been studied by three-step excitation using three lasers [32–34]. However, few studies have used three lasers to examine the photodynamics of photochromic materials.

Photochromic compounds within the nanocavities of molecules such as cyclodextrins (CDs) and crown ethers have been shown to exhibit reversible and efficient photochromic reactions [35–42]. The effect of complexing diarylethene derivatives in the cavity of CDs on their photochromism has been investigated [37,43,44]. We previously studied the TPI of the diarylethene derivative 1,2-bis (2,4-dimethyl-5-phenyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-

cyclopentene (**2**) in water and acetonitrile (AN) in the presence of various cyclodextrins (α -CD, β -CD, m β -CD, and γ -CD) using 266 nm laser irradiation [45]. TPI of **2** was observed upon irradiation with 266-nm light in the presence of all varieties of CD. As the concentration of m β -CD was increased, the TPI of **2** suppressed its photochromic reaction, resulting in a longer fluorescence lifetime and increased ionization quantum yield (Φ_{ion}). Consequently, we determined that the addition of 50 mM m β -CD is advantageous to increase Φ_{ion} of **2**, and that the photochromic reaction of **2** is affected by the concentration of CD, which in turn influences Φ_{ion} . Evaluation of the most stable structures formed by the inclusion of **2** in CDs by theoretical calculations revealed that the **2**/ α -CD complex should be the easiest to photoionize because a large area of each molecule of **2** protruded into the solvent [45].

The photochromism of materials can be influenced by inclusion into the cavity of host species, and also by photoionization, but this has seldom been investigated using multiple lasers. Here we investigate the resonant photoionization of H_2O/AN solutions of **1** using one-laser (266 nm), two-color two-laser (266 and 532 nm), and three-color three-laser (266, 532 and 355 nm) flash photolysis. Because **1** has poor solubility in water, we added CDs to form **1**/CD inclusion complexes that dissolve in water. With regard to the ionization of **1**, if the ionized species can easily be stabilized by solvent molecules, ionization should be promoted and Φ_{ion} should increase [45]. Therefore, ionization of **1** is investigated here using CDs with different cavity sizes to determine the CD that allows the most efficient ionization of **1**. From the transient absorption (Δ Abs.) of the hydrated electrons (e_{aq}^{-}) in these systems observed by multi-color multi-laser flash photolysis measurements, we calculate Φ_{ion} and the ionization yield (Y_{ion}) of **1**. Understanding the interplay between the TPI and photochromism of **1** induced by three-color three-laser irradiation may aid in exploiting its photobehavior in optical switches and actuators.

2. Experimental

1 (Tokyo Chemical Industry, Co., Ltd., Tokyo, Japan), AN (spectroscopic grade, Wako, Osaka, Japan), α - and β -CD (Nacalai Tesque, Kyoto, Japan) and γ -CD (Kanto Chemical Co., Tokyo, Japan) were used as received. Solutions of 1 and each CD with concentrations of 2.1 × 10⁻⁴ and 10 × 10⁻³ M, respectively, were mixture in H₂O/AN (9:1 v/v). Therefore, concentration of 1 in H₂O/AN (9:1 v/v) was 2.1 × 10⁻⁵ M. The NMR measurement was carried out using the concentration of 2.1 × 10⁻³ M because detection of ¹H NMR spectra is difficult for the low concentration.

Multi-color multi-laser flash photolysis was performed using the fourth harmonic (266 nm) of a Nd:YAG laser (Spectra-Physics (manufactured in U.S.A.), GCR-130-10; laser pulse energy (I) = 10mJ pulse⁻¹, full width at half-maximum (FWHM)=5 ns, and fluence (F) = 80 mJ cm⁻² pulse⁻¹), the third harmonic (355 nm) of a Nd:YAG laser (Spectra-Physics, DCR-2A; $I = 30 \text{ mJ pulse}^{-1}$, FWHM = 5 ns, and $F = 106 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$) and the second harmonic (532 nm) of a Nd:YAG laser (Spectra-Physics, PRO-250-10; $I = 500 \text{ mJ pulse}^{-1}$, FWHM = 5 ns, and $F = 159 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$) as the first, third and second lasers, respectively. The power of each laser was measured by a laser power meter (Gentec ED-200UV). Single-laser irradiation (1-LFP) was performed using a quadrupled YAG laser (266 nm) [45]. Two-color two-laser irradiation (2-LFP) at 266 and 532 nm simultaneously was also conducted for each sample solution. Three-color three-laser irradiation (3-LFP) at 266, 532 and 355 nm was applied to each sample solution with a delay time of 2 µs between each laser pulse. Thus, there was a delay time of 4 µs between the first 266 nm pulse and third 355 nm pulse applied to the sample solution. A schematic of the setup is illustrated in Fig. 1.



Fig. 1. Multi-color multi-laser irradiation system for photoionization of 1/CDs.

Benzophenone (Bp) was used as an actinometer to measure photon density. In previous studies of the ionization of aromatic molecules to radical ions, we measured the Δ Abs. of e^-_{aq} at 720 nm to determine the reaction kinetics [24,45]. In the case of 1-LFP and 2-LFP, we used the value of Δ Abs. at 1.5 µs after laser irradiation. For 3-LFP, we used the value of Δ Abs. at 8.5 µs after the initial laser irradiation. These delays were chosen because immediately after excitation, the absorption of e^-_{aq} was overlapped by a relatively short-lived triplet absorption of organic molecules. The hydrated electron absorption featured long microsecond lifetime component in line with that observed in previous reports [46]. The hydrated electron density $[e^-_{aq}]$ determined from 1-LFP measurements was used to calculate Φ_{ion} (Eq. (1)) for **1** as follows [45]: for a 266 nm pulse, time delay of 2 µs, 355 nm pulse, time delay of 2 µs, 532 nm pulse.

$$2\Phi ion = \frac{[e_{aq}]'}{[photon]} = \frac{\frac{\Delta Abs._{720}}{c_{720} \cdot l}}{\frac{\Delta Abs._{525}}{c_{525} \times l}} / \frac{1}{Abs._{266}} = \frac{[e_{aq}]}{[^{3}Bp^{*}]} / \frac{1}{Abs._{266}}$$
(1)

Here, $[e_{aq}]'$ is used to indicate the concentration of hydrated electrons following normalization by the absorption of **1** at 266 nm. The factor 2 is an account for the absorption of two photons. Additionally, $[e_{aq}]$ determined from 2-LFP and 3-LFP measurements was used to calculate Y_{ion} (Eq. (2)).

$$Y_{\text{ion}} = \frac{[e_{aq}]}{[1]} = \frac{{}^{\Delta}\text{Abs.}_{720} / {}_{\epsilon_{720}} \times l}{{}^{\text{Abs.}_{266}} / {}_{\epsilon_{266}} \times l}$$
(2)

 Y_{ion} is equal to $[e_{aq}]$ divided by the concentration of **1** ([**1**]). Cyclization yield $(Y_{o \rightarrow c})$, cycloreversion yield $(Y_{c \rightarrow o})$, cyclization quantum yield $(\Phi_{\text{o}\rightarrow\text{c}})$ and cycloreversion quantum yield $(\Phi_{\text{c}\rightarrow\text{o}})$ were calculated from the concentrations of the CL and OP forms of **1**, respectively, using 3-LFP with a delay time of $4 \mu s$ (Eqs. (3)–(6), respectively). Here, [CL], [OP] and $\Delta Abs._{580}$ indicate the $\Delta Abs.$ at 580 nm, concentration of CL and OP, respectively. Δ Abs. for the OP and CL forms of 1 was determined using the wavelength of the absorption peak of CL of 1. Formation of OP of 1 was calculated as the difference between ΔAbs . of CL of **1** 2.5 μs after laser irradiation at 266 and 532 nm; that is, the decrease of ΔAbs . of CL of **1** caused by 532 nm laser irradiation ($\Delta\Delta$ Abs.₅₈₀ = $\Delta Abs_{.580}^{266} - \Delta Abs_{.580}^{532}$). For 355 nm laser irradiation, ΔAbs . was determined 10.0 µs after the laser pulse. As above, this was to avoid the influence of triplet absorption. Bp and fullerene (C_{60}) were used as actinometers to measure the photon density in these experiments.

$$\Upsilon_{\mathbf{o}\to\mathbf{c}} = \frac{[\mathsf{CL}]}{[1]} = \frac{\Delta_{\mathsf{Abs}} \cdot _{580} / _{\varepsilon_{580}} \times \mathbf{l}}{\frac{\mathsf{Abs}}{\mathsf{Abs}} \cdot _{266} / _{\varepsilon_{266}} \times \mathbf{l}}$$
(3)

$$\Upsilon_{c \to o} = \frac{[OP]}{[1]} = \frac{\Delta Abs_{.580} /_{\epsilon_{580}} \times l}{Abs_{.266} /_{\epsilon_{266}} \times l}$$
(4)

$$2\Phi o \to c = \frac{[CL]'}{[photon]} = \frac{\frac{\Delta Abs_{580}}{\frac{E_{590}\times 1}{E_{595}\times 1}} \Big/_{Abs.^{1}_{266}}}{\frac{\Delta Abs_{525}}{E_{525}\times 1} \Big/_{Abs.^{Bp}_{266}}} = \frac{[CL]/_{Abs.^{1}_{266}}}{[^{3}Bp^{*}] \Big/_{Abs.^{Bp}_{266}}}$$
(5)

$$2\Phi c \to o = \frac{[OP]'}{[photon]} = \frac{\frac{\Delta\Delta Ab_{550}}{c_{580}\times 1}}{\frac{\Delta Ab_{532}}{c_{738}\times 1}} / \frac{Ab_{5}^{1}}{Ab_{5}^{1}} = \frac{[OP]/_{Abs}^{1}}{[{}^{3}C_{60}^{*}]/_{Abs}^{0}}$$
(6)



1/α-CD1

Fig. 2. Minimum-energy structure of an inclusion complex of 1 (space-filling molecule) and α -CD (ball-and-stick molecule) calculated by MM2.

The ionization potential (IP) of **1** was calculated using cyclic voltammetry (CV) conducted with an electrochemical analyzer (ALS/CHC Instruments, 600B). Tetrabutylammonium perchlorate (0.1 M) in AN was used as the electrolyte and the reference electrode was Ag/AgNO₃ (10×10^{-3} M). The IP of **1** was determined from its oxidation potential according to a previous report [33]. Absorption and fluorescence spectra were measured at room temperature by a spectrophotometer (Hitachi, U-3310) and spectrofluorometer (Perkin Elmer, LS 55), respectively. ¹H NMR spectra were measured on a 400-MHz spectrometer (JEOL, Datum JNM-ATUM) with a concentration of **1** of 2.1×10^{-3} M and CD concentrations of 0.5, 1, 3, 5 and 10×10^{-3} M.

To estimate the extent of inclusion of **1** into each CD, the complexes were subjected to geometry optimization to the most energetically stable structure using MM2 (CS Chem3D). α -CD with a fully included **1** molecule was used as the starting geometry.

3. Results and discussion

3.1. Structure of the 1/CD complexes

We calculated the most stable structures formed by the inclusion of **1** into the various CDs using MM2; the calculated structure for $1/\alpha$ -CD is presented in Fig. 2. The OP form of **1** is 8.5 Å along the long axis and 6.4 Å along the short axis, while the CL form of **1** is 10.0 Å along the long axis and 5.6 Å along the short axis. The calculation results indicate that in the α -CD inclusion complex, only one of the thiophene rings of **1** inserts into α -CD and the maleic anhydride group protrudes into the solution. In the case of β -CD, **1** embeds deeper into the CD cavity than in α -CD. γ -CD includes **1** fully, reflecting its larger cavity size. The cavity sizes of α -, β -, γ -CD are 4.5, 7.0, and 8.5 Å, respectively [45].

The ¹H NMR spectrum of **1** (2.1×10^{-3} M, $30 \circ$ C, 400 MHz) in deuterated AN without any CDs contained peaks at approximately δ 2.25 and 2.23 ppm that were assigned to the methyl protons on the thiophene ring of **1** in the antiparallel and parallel

conformations, respectively (Fig. 3). The intensity ratio of this doublet indicates that the two 1 conformations exist in almost equal amounts in deuterated AN; the ratio of antiparallel to parallel conformations was calculated to be 0.89:1.00. In the presence of CDs (0.5, 1, 3, 5 and 10 \times 10 $^{-3}$ M), the ^1H NMR spectra of 1 exhibited peaks at approximately δ 2.25 and 2.22 ppm. The peak attributed to the parallel conformation of **1** shifted slightly upfield in the presence of CDs (Fig. 3). Additionally, the ratio of the antiparallel conformation of **1** increases with the concentration of α -. β - and γ -CD (Fig. 4). Because the parallel conformation of **1** in solution was assumed to be constant with increasing CD concentration, this suggests that the formation ratio of 1/CD inclusion complexes increased with CD concentration. The ratios of antiparallel to parallel conformations of **1** in the presence of different types and concentrations of CDs determined from the ¹H NMR data are listed in Table 1.

3.2. Steady-state absorption spectra

Fig. 5 shows the steady-state absorption spectra of 1 in AN. The maximum absorption peak of OP 1 was observed at ~335 nm. After irradiation at 254 nm, new absorption peaks appeared at ~380 and ~560 nm, indicating isomerization from OP to CL 1. Isomerization of 1 upon exposure to 254 nm irradiation was also observed in the presence of α -, β - and γ -CD (data not shown). The absorption peaks of CL 1 in the presence of CDs appeared at ~390 and ~580 nm. Compared with α - and γ -CD, in the presence of β -CD the absorption band of CL 1 at ~580 nm was weak.

3.3. TPI of 1 with one-laser irradiation

We measured the transient absorption at 720 nm after irradiating each H_2O/AN (9:1 v/v) solution of **1**/CD with a 266-nm laser (Fig. 6). The decay showed an initial rapid (nanosecond) decay followed by a longer component with a microsecond lifetime. Under these conditions e^-_{aq} and radical



Fig. 3. ¹H NMR spectra (400 MHz, 30 °C) of the methyl protons on the thiophene rings of $\mathbf{1}$ (2.1 × 10⁻³ M) in deuterated AN (without CD, top) and $\mathbf{1}$ in the presence of different concentrations of α -, β - and γ -CD (left, middle and right, respectively) in deuterated H₂O/deuterated AN (9:1 v/v).



Fig. 4. Dependence of the percentage of antiparallel conformation of 1 (2.1×10^{-4} M) on the concentration of CDs in deuterated H₂O/deuterated AN (9:1 v/v). (A) α -CD, (B) β -CD, and (C) γ -CD.

cation pairs rapidly form within the duration of the laser pulse, through the following reaction:

 $S_0(OP) + h\nu \quad (\lambda = 266 \text{ nm}) \to S_1(OP) + h\nu \quad (\lambda = 266 \text{ nm}) \to S_n \to \mathbf{1}^{*+} + e_{aq}^- \text{(TPI, 266 nm)}$ (7)

Table 1

Chemical shifts (δ) of **1** (2.1 × 10⁻³ M) in deuterated AN (without CDs) and **1** (2.1 × 10⁻⁴ M) in the presence of different types and concentrations of CDs in deuterated H₂O/deuterated AN (9:1 v/v).

CD	Concentration (10 ⁻³ M)	δ/antiparallel (ppm)	δ/parallel (ppm)	Ratio of antiparallel: parallel
Non	0	2.25	2.23	0.89:1.00
α-CD	0.5 1 3 5 10	2.25 2.25 2.25 2.25 2.25 2.25	2.22 2.21 2.21 2.22 2.22 2.22	0.91:1.00 1.02:1.00 1.12:1.00 1.19:1.00 1.27:1.00
β-CD	0.5 1 3 5 10	2.25 2.25 2.25 2.25 2.25 2.25 2.25	2.22 2.22 2.22 2.22 2.22 2.22	0.91:1.00 1.06:1.00 1.14:1.00 1.22:1.00 1.31:1.00
γ-CD	0.5 1 3 5 10	2.25 2.25 2.25 2.25 2.25 2.25	2.22 2.22 2.22 2.22 2.22 2.23	0.91:1.00 0.93:1.00 1.11:1.00 1.21:1.00 1.48:1.00



Fig. 5. Absorption spectra of the open form (solid line) and closed form (dashed line) of **1** in AN. The inset shows an expansion of the region 470-700 nm.

Although the solvent included around 10% AN, we considered that reactions of the hydrated electron with the solvent had a negligible effect on the kinetics of e^-_{aq} . The absorption maximum of e^-_{aq} occurs at 720 nm, and when AN alone was used as the solvent no changes in the absorption at this wavelength at were observed, which supports the formation of a hydrated electron. Our previous studies have suggested that the absorption at 720 nm is partially overlapped by short-lived triplet absorption from other organic molecules [24], which contribute to the initial rapid decay of the absorption. We attribute the long-lived component of the decay to neutralization of the e^-_{aq} [24].

The TPI of **1** was confirmed from its singlet excitation energy (S₁) and IP. S₁ and IP were calculated from the maximum fluorescence of the **1**/CD complexes in H₂O/AN (9:1 v/v) [19] and CV measurements, respectively. The maximum fluorescence of **1**/CDs in H₂O/AN (9:1 v/v) was at ~420 nm, so S₁ was calculated to be 3.0 eV. CV measurements in AN-based electrolyte gave a redox potential E^{ox} of 0.34 eV, so the IP of **1** was calculated to be 6.3 eV using the conversion formula $(1.473 \pm 0.027) E^{\text{ox}} + (5.821 \pm 0.009)$ [47]. In H₂O/AN (9:1 v/v) with CDs, the IP of **1** decreased by



Fig. 6. Time profiles of transient absorption of 1/CD complexes observed at 720 nm after a 5 ns laser flash at 266 nm. (A) α -CD, (B) β -CD, and (C) γ -CD. The insets show enlarged images.

approximately 1.0 eV to 5.3 eV because of solvation effects. This IP is higher than the one-photon energy of 266 nm light (4.7 eV), which implies that ionization requires two or more photons (Fig. 7).

 Φ_{ion} of 1 in the presence of α -, β - and γ -CD were calculated to be 5.8 \pm 0.3%, 5.6 \pm 0.3% and 1.5 \pm 0.1%, respectively (Table 2). Φ_{ion} was lowest in the presence of γ -CD, which implies that



Fig. 7. Energy diagram for TPI of **1** under 266 nm irradiation (1-LFP) and simultaneous irradiation at 266 and 532 nm (2-LFP).

Table 2

Ionization quantum yields (Φ_{ion}^{266}) and ionization yields (Y_{ion}^{266} and $Y_{ion}^{266+532}$) of 1 (2.1×10^{-5} M) in the presence of various CDs (10×10^{-3} M) in H₂O/AN (9:1 v/v).

CD	$\Phi_{ion}{}^{266}$ (%)	Y_{ion}^{266} (%)	$Y_{\rm ion}^{266^*532}(\%)$	$Y_{\rm ion}^{266^*532}/Y_{\rm ion}^{266}$
α-CD	$\begin{array}{c} 5.8 \pm 0.3 \\ 5.6 \pm 0.3 \\ 1.5 \pm 0.1 \end{array}$	1.8	5.9	3.3
β-CD		2.5	7.1	2.8
γ-CD		1.4	3.8	2.7



Fig. 8. Fluorescence spectra (normalized at 490 nm) of $1~(2.1\times10^{-5}\,M)$ in the presence of different CDs ($10\times10^{-3}\,M).$



Fig. 9. Time profiles of transient absorption of $1/\alpha$ -CD observed at 720 nm after flash photolysis using 266 and 532 nm lasers. The insets shows (Left) enlarged image and (Right) plot of log($\Delta\Delta$ Abs.₇₂₀) against log *I* for $1/\alpha$ -CD in H₂O/AN (9:1 v/v).



Fig. 10. Time profile of transient absorption of $1/\alpha$ -CD observed at 720 nm after LFP with various pulse configurations. Inset is a plot of log ($\Delta\Delta$ Abs.720) against log *I* during LFP of $1/\alpha$ -CD in H₂O/AN (9:1 v/v).

Table 3

Ionization yields (Y_{ion}) of $1~(2.1\times10^{-5}\,M)$ in the presence of various CDs $(10\times10^{-3}\,M)$ in $H_2O/AN~(9:1~v/v)$ using different pulse configurations during 3-LFP.

CD	Yion ^{266+non+non} (%)	Y _{ion} ^{266+non+355} (%)	Y _{ion} ²⁶⁶⁺⁵³²⁺³⁵⁵ (%)	$Y_{ion}^{266+532+355/}$ $Y_{ion}^{266+non+355}$
α-CD	1.9	3.1	5.0	1.6
β-CD	0.5	1.7	2.3	1.4
γ-CD	0.6	0.9	1.6	1.8

Table 4

Cyclization yields ($Y_{o \rightarrow c}$ and $Y_{c \rightarrow o}$) cyclization quantum yields ($\Phi_{o \rightarrow c}$ and $\Phi_{c \rightarrow o}$) of **1** (2.1 × 10⁻⁵ M) in the presence of various CDs (10 × 10⁻³ M) in H₂O/AN (9:1 v/v).

CD	$\frac{Y_{o\rightarrow c}^{266}}{(\%)}$	$Y_{c \to o}^{532}$ (%)	$\frac{Y_{o\rightarrow c}^{355}}{(\%)}$	Ring opening (%)	$\Phi_{\text{o}\rightarrow\text{c}}{}^{266}$	$\Phi_{c\too}{}^{532}$
α-CD	13.6	8.5	67.8	62.5	0.61 ± 0.03	$\textbf{0.15} \pm \textbf{0.01}$
β-CD	18.2	3.8	68.9	20.9	$\textbf{0.95} \pm \textbf{0.01}$	$\textbf{0.07} \pm \textbf{0.01}$
γ-CD	7.1	5.1	9.3	71.8	0.37 ± 0.02	$\textbf{0.11} \pm \textbf{0.01}$



Fig. 11. Photoionization of 1 using 266 + 532 + 355 nm irradiation with a delay time of 2 μ s between each pulse.



Fig. 12. Transient absorption spectrum of $1/\alpha$ -CD observed at 580 nm after 266+532+355 nm irradiation with a delay time of 4 µs between each pulse. The inset show enlarged image.

isomerization of **1** could occur more readily in γ -CD than in the other CDs because its cavity is larger. To confirm that this is the case, we measured fluorescence spectra of **1** in the presence of the various CDs (Fig. 8). The fluorescence of the CL isomer was observed at ~540 nm, and normalized at 490 nm to allow comparison. The fluorescence intensity of CL **1** was higher in the presence of γ -CD compared with that in the presence of the other CDs. This is because the isomerization of **1** is not strongly inhibited in the γ -CD cavity, which is larger than those of the other

CDs. These results suggest that Φ_{ion} of **1** may be maximized by inhibiting isomerization.

3.4. TPI of 1 with two-color two-laser irradiation

Interestingly, the Δ Abs. $_{720}$ of e^{-}_{aq} increased compared with that for 1-LFP during TPI with simultaneous irradiation by 2-LFP at 266 and 532 nm with laser intensities of 10 and 500 mJ pulse⁻¹, respectively (Fig. 9). Y_{ion} of **1** in the presence of α -, β - and γ -CD were 5.9%, 7.1% and 3.8%, respectively, which are much higher than the Y_{ion} of 1.8%, 2.5% and 1.4%, respectively, obtained during TPI by 1-LFP (10 mJ pulse⁻¹) (Table 2). Formation of e^{-}_{aq} was not observed during laser photolysis with 532 nm irradiation alone (500 mJ pulse⁻¹).

We next investigated the dependence of Y_{ion} of **1** on *I* of the 532 nm laser pulse. The slope of a plot of log *I* against log ($\Delta\Delta$ Abs. $_{720} = \Delta$ Abs. $_{720}^{266*532} - \Delta$ Abs. $_{720}^{266}$) was approximately 1 (inset of Fig. 9). This suggests that TPI occurred from **1** in a singlet excited state; that is, **1** (S_n) was generated from the 532 nm excitation of **1** (S_1) (Fig. 7). The energy level achieved upon excitation by 2-LFP is estimated to be 5.3 eV by addition of the singlet state energy ($E_{S1} = 3.0 \text{ eV}$) of **1** (S_1) and the 532 nm laser photon energy (2.3 eV). An excitation energy of 5.3 eV is sufficient to ionize **1** in H₂O/AN (9:1 v/v). Thus, the formation of e_{-aq} occurs through the two-step two-photon resonant excitation of the $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_n$ transitions when using 266 and 532 nm laser pulses, respectively (Eqs. (8) and (9)).

$$S_0(OP) + h\nu \quad (\lambda = 266 \text{ nm}) \rightarrow S_1(OP) + h\nu \quad (\lambda = 266 \text{ nm}) \rightarrow S_n \rightarrow \mathbf{1}^{\bullet^+} + e^-_{aq}$$
(8)

$$S_0(OP) + h\nu \quad (\lambda = 266 \text{ nm}) \rightarrow S_1(OP) + h\nu \quad (\lambda = 532 \text{ nm}) \rightarrow S_n \rightarrow \mathbf{1}^{\bullet^+} + e^-_{aq}$$
(9)

3.5. Photoionization of 1 with three-color three-laser irradiation

The transient absorption of e_{aq}^- of the **1**/CD complexes was observed following 266 nm irradiation with the first laser and 355 nm irradiation with the third (*i.e.*, 266 + non + 355 nm) with a delay time of 4 µs between laser pulses, as shown in Fig. 10 (black line). The formation of e_{aq}^- in this case is described in Eqs. (10) and (11) below. For these experiments, Y_{ion} was calculated to be 3.1%, 1.7% and 0.9% in the presence of α -, β - and γ -CD, respectively (Tables 3 and 4).

$$S_0(OP) + h\nu \ (\lambda = 266 \text{ nm}) \rightarrow S_1(OP) \rightarrow S_0(OP)$$
(10)

$$\begin{split} S_{0}(OP) + h\nu & (\lambda = 355 \text{ nm}) \to S_{1}(OP) + h\nu & (\lambda = 355 \text{ nm}) \to S_{n} \to \mathbf{1^{\bullet^{+}}} + e^{-}_{aq} & (TPI, 355 \text{ nm}) \end{split}$$

The transient absorption of e_{aq} of the 1/CD systems following excitation with sequential 266, 532 and 355 nm laser pulses with a delay time of 2 µs between each pulse was then examined (blue line in Fig. 10). Y_{ion} of 1 in the presence of α -, β - and γ -CD using this 3-LFP configuration were 5.0%, 2.3% and 1.6%, respectively, which are higher than the Y_{ion} of 3.1%, 1.7% and 0.9%, respectively, obtained during photoionization by the 266 + non + 355 nm laser pulses above. The increase of photoionization efficiency (Y_{ion}²⁶⁶+⁵³²⁺³⁵⁵/Y_{ion}^{266+non+355}) of 1 was particularly large in the presence of γ -CD. This suggests that Y_{ion} of 1 increased because 1 was cyclized upon the first 266nm laser excitation (Eq. (12)), and then underwent cycloreversion upon the second 532 nm laser excitation (Eq. (13)). Photoionization probably occurs upon 355 nm laser irradiation (Eq. (14)).

$$S_0(OP) + h\nu (\lambda = 266 \text{ nm}) \rightarrow S_1(OP) \rightarrow S_0(CL) (cyclization)$$
 (12)

$$S_0(CL) + h\nu (\lambda = 532 \text{ nm}) \rightarrow S_1(CL) \rightarrow S_0(OP) (cycloreversion)$$
 (13)

$$S_0(OP) + h\nu \quad (\lambda = 355 \text{ nm}) \rightarrow S_1(OP) + h\nu \quad (\lambda = 355 \text{ nm}) \rightarrow S_n \rightarrow \mathbf{1}^{\bullet+} + e^-_{ag} \text{ (TPI, 355 nm)}$$
(14)

We next investigated the dependence of Y_{ion} of **1** on laser pulse energy at 532 nm, as for 2-LFP above. The slope of a plot of log *I* against log ($\Delta\Delta$ Abs. ₇₂₀ = Δ Abs. ₇₂₀²⁶⁶⁺⁵³²⁺³⁵⁵– Δ Abs. ₇₂₀^{266+non+355}) was approximately 1 (Fig. 10, inset). This suggests that an increase in photoionization occurred through the three-step excitation, which can be attributed to the cycloreversion of **1** upon 532 nm irradiation with the second laser (Fig. 11).

3.6. Mechanism of the cyclization reaction of 1 with 3-LFP

To understand the observed increase of photoionization efficiency using 3-LFP, we investigated the cyclization reaction of 1 during 3-LFP to show the mechanism of cyclization. The steady-state absorption peak of the CL isomer of 1 in the CDs is observed at \sim 580 nm in H₂O/AN (9:1 v/v). Additionally, changes in the transient absorption of the 1/CD systems were observed at 580 nm [19] during 3-LFP with 266 + 532 + 355 nm laser irradiation and a delay time of $4 \mu s$ between each pulse, as shown in Fig. 12. This suggests that 1 was cyclized upon 266 nm irradiation with the first laser, underwent cycloreversion upon 532nm irradiation with the second laser and then cyclized again upon 355 nm irradiation with the third laser. $Y_{o \rightarrow c}$ and $Y_{c \rightarrow o}$ determined for **1** using 3-LFP are listed in Table 3. The molar absorption coefficient of 1 in the presence of β -CD was assumed to be the same as that for **1** in the presence of α -CD. The percentages of **1** that underwent ring opening in the presence of α -, β - and γ -CD were 62.5%, 20.9% and 71.8%, respectively. These values were determined from the ratios of $Y_{0\to c}^{266}$ to $Y_{c\to 0}^{532}$, and indicate the reformation of OP **1** using 532 nm laser irradiation. This suggests that the observed increase of photoionization efficiency in the presence of CDs was caused by the ring opening of **1** induced by the second laser pulse (532 nm).

 $\Phi_{\mathsf{o} \to \mathsf{c}}$ and $\Phi_{\mathsf{c} \to \mathsf{o}}$ for 1 determined for the first and second laser pulses at 266 and 532 nm, respectively, in the presence of the different CDs are presented in Table 3. A previous report found that $\Phi_{o \rightarrow c}$ of **1** in solution decreased with increasing solvent viscosity, and was calculated to be 0.13 in *n*-hexane from the time dependence of the spectral changes under steady-state irradiation [16]. In addition, the cyclization of **1** is affected by solvent polarity; the absorption spectra of 1 in *n*-hexane and AN are different. In this study, $\Phi_{o \rightarrow c}$ of the 1/CD complexes in H₂O/AN (9:1 v/v) were much higher than 0.13. This is because inclusion of **1** in CDs inhibits its isomerization. Furthermore, 1 undergoes two-photon absorption upon nanosecond-pulsed laser irradiation. As a result, cyclization occurs in the S_n state that is formed by two-photon absorption (Fig. 11). In contrast, the cycloreversion reaction of **1** is hardly affected by the polarity and viscosity of the solvent. Therefore, cycloreversion of $\mathbf{1}$ occurs from the S_1 state through one-photon absorption. This is further confirmed by the dependence of Y_{ion} of 1 on the pulse energy of the 532 nm laser pulse during 3-LFP (inset of Fig. 10).

Overall, these results suggest that the photochromism of **1** can be influenced by three-color three-laser irradiation. Harada and coworkers [42,48–50] designed a photoresponsive supramolecular actuator using host–guest interactions and the photoswitching ability of a hydrogel containing a CD. Therefore, our research on the ability of flash photolysis with multiple lasers to influence the interplay between the photoionization and photochromism of **1** may be useful for realizing control of materials that respond to external stimuli for applications like optical memory and molecular motors.

4. Conclusion

Photoionization of **1** was observed upon irradiation with onelaser, two-color two-laser and three-color three-laser light in the presence of CDs and quantified by determination of $[e_{aq}]$. $[e_{aq}]$ generated upon TPI using two-color two-laser irradiation was higher than that obtained following one-laser irradiation, suggesting that the second step involving one-photon resonant excitation from **1** (S_1) to **1** (S_n) made a substantial contribution to Y_{ion} of **1**. $[e_{aq}]$ generated by photoionization using three-color three-laser irradiation (266, 532 and 355 nm) with a delay time of $2 \mu s$ between each pulse was higher than that following 2-LFP at 266 and 355 nm with a delay time of $4 \mu s$ between pulses, suggesting that photoionization occurred by a three-step excitation process in this case. The observed increase of the photoionization efficiency of 1 upon 532 nm irradiation was caused by the ring opening of **1** and was influenced by the cavity size of the CD. The photoionization efficiency of **1** can be increased by controlling its ability to isomerize through formation of inclusion complexes with CDs.

Conflicts of interest

The authors report no conflicts of interest.

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